Superconducting properties of nanocrystalline MgB_2

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Abstract. Nanocrystalline MgB_2 produced by mechanical alloying has been shown to exhibit enhanced superconducting properties such as increased pinning and higher critical currents. However, the effects of the synthesis process on the intrinsic superconducting properties have not been addressed yet. We have investigated the superconducting gap structure of nanocrystalline MgB_2 pellets synthesized by high-energy ball milling employing specific heat measurements. We found that the larger σ-gap decreased whereas the smaller π-gap slightly increased in ball milled MgB_2 as compared to bulk samples synthesized along the standard routes. The data show that the ball milling process introduces defects that enhance the interband scattering similar to irradiation with neutrons. The reduction of the σ-gap explains the lower superconducting transition temperature of 33 K.

1. Introduction

Since the discovery of superconductivity at 40 K in MgB_2 [1] many attempts have been reported to improve the material properties that are important for potential applications. Unlike the high-T_c cuprate superconductors where the current carrying capacity is limited by weak links across grain boundaries, the critical current in MgB_2 is mainly determined by its flux pinning properties. Various investigators have therefore focused their attention onto the controlled increase of the number of pinning centers by introducing disorder and defects using, for example, irradiation techniques [2] or the implementation of nanometer-sized particles of Si, C, SiC, TiB, or YB_4 into polycrystalline MgB_2 [3]. An increase of the upper critical field was in fact observed in bulk samples as well as in thin films showing a high degree of disorder in the boron planes [4]. Alternatively, the pinning properties of MgB_2 can be improved by increasing the density of grain boundaries and/or bulk defects by reducing the average grain size into the nanometer range. Nanocrystalline powders can be produced by mechanical alloying the starting materials (Mg and B) using high-energy ball milling [5]. The partial reaction of Mg and B to MgB_2 during the milling process is completed by subsequent hot pressing resulting in very dense ceramic pellets with distinctly enhanced pinning in the superconducting state. A combination of both routes, the addition of oxide particles into a nanocrystalline MgB_2 matrix has led to a significant improvement of the extrinsic superconducting properties [6].

The introduction of disorder and defects, however, has also an effect on other relevant parameters of the superconducting state. First of all, in many instances the critical temperature, T_c, is dramatically reduced (by up to 20 % of the maximal $T_c \simeq 40$ K) as defects and disorder are implemented to enhance H_{c2}. This defect-induced decrease of T_c was discussed in an early review on MgB_2 [7] in analogy to the reduction of T_c in ion-irradiated superconducting Nb-Ge films [8]. Of more fundamental interest, however, is the influence of impurities, disorder, and defects on the superconducting gap structure of MgB_2. The possible existence of multiple superconducting gaps was first suggested by Liu et al. from a first-principle calculation of the band structure and the electron-phonon coupling in MgB_2 [9] and later confirmed by a number of experimental investigations, preferentially heat capacity measurements [10] and tunneling spectroscopy [11]. The two superconducting gaps are correlated via interband scattering and they close at the same critical temperature. The existence of two types of supercarriers and two gaps of different magnitude is the origin of the very peculiar temperature dependence of the heat capacity, $C_p(T)$, in the superconducting state which deviates from the typical T-dependence of C_p following from the BCS theory [12]. The larger gap was assigned to the σ-band the carriers of which couple strongly to the E_{2g} phonons in the boron planes whereas the smaller gap appears in the π-band and its carriers couple only weakly to phonons. A direct experimental proof for this assignment was given recently [13]. From a theoretical point of view the problem of multi-band superconductivity was considered already several decades ago and it was found that the two superconducting gaps close

at the same T_c as a consequence of interband coupling between electrons in different bands mediated by phonons [14].

It is the main objective of this work to investigate the effects of the small grain size of nanocrystalline MgB_2 and the impurities and defects introduced by the high-energy ball milling procedure on the intrinsic superconducting properties and, in particular, on the superconducting gaps of MgB_2. Magnetic, electrical transport, and heat capacity experiments are conducted and the values for the superconducting gaps are extracted from the temperature dependence of the specific heat. We show that the larger σ-gap is reduced by more than 40 % in nanocrystalline MgB_2 as compared with samples prepared using standard synthesis procedures.

The experimental setup is described in section 2 and the results are presented in section 3. The conclusions are presented and discussed in the last section.

2. Experimental techniques

Nanocrystalline MgB_2 was prepared by high-energy ball milling of the precursor materials Mg (99.8 %, particle size 250 μm) and B (99.9 %, particle size 1 μm) as described in more detail elsewhere [5]. The milling was conducted in Ar atmosphere using jar and balls made from tungsten carbide (WC). After 20 hours of milling time Mg and B partially reacted (cold alloying) to form MgB_2. The x-ray spectrum shows already some peaks assigned to MgB_2 together with diffraction peaks from Mg and WC. The reaction was completed by hot uniaxial pressing at 973 K / 640 MPa for 10 minutes. This treatment resulted in a complete conversion of Mg and B to MgB_2 with only minor traces of impurity phases left (3 % MgO and 0.3 % WC, Fig. 1 and [5]). The coherent scattering length for the MgB_2 was estimated from the x-ray spectra as 30 nm and the MgB_2 particle size (from SEM) is 40 to 100 nm.

The physical properties and the superconducting transition are characterized by ac magnetic susceptibility, resistivity, thermoelectric power, and specific heat measurements. The ac susceptibility was determined by measuring the mutual inductance of a dual coil system attached to the sample employing the LR700 Mutual Inductance/Resistance Bridge (Linear Research). The resistivity was measured in four-lead configuration with the same device. For the thermoelectric power experiments we have used a home made high-resolution ac measurement technique. The heat capacity was determined by a relaxation technique using the Physical Property Measurement System (Quantum Design).

3. Results and discussion

The electrical resistivity (Fig. 2) displays the characteristic temperature dependence of MgB_2 with a low ratio of the residual (R just above T_c) and room temperature resistance, RRR=1.38, which is typical for MgB_2 samples with a high concentration of defects or impurities [15]. Enhanced scattering at the grain boundaries should also

contribute to an increase of the residual resistance and lower the RRR-values. The inset of Fig. 2 shows the ac susceptibility near the superconducting phase transition. The T_c=33 K defined by the midpoint of the drop of χ_{ac} is significantly lower than the 39 K known for bulk MgB_2. The width of the transition of only 0.6 K indicates good sample uniformity which is important for the discussion of the thermodynamic properties.

The thermoelectric power, S(T), is less sensitive to grain boundaries and reflects the intrinsic material properties better than the resistivity. The thermoelectric power of the nanocrystalline MgB_2 (Fig. 3) is well comparable with data obtained from "standard" MgB_2 [16, 17]. The inset of Fig. 3 expands the temperature range close to T_c and reveals the sharp drop of S(T) to zero at the superconducting transition. The change of slope above 200 K and the high-temperature value of about 9 μV/K is very similar to the properties of bulk samples. The major difference is the lower T_c value that indicates an effect of the grain size and the ball milling procedure on the extrinsic superconducting properties.

The superconducting gaps of MgB_2 can be determined from thermodynamic quantities such as the specific heat. It was demonstrated that the particular two-gap structure is responsible for the peculiarities of the heat capacity observed at low T and close to T_c [10]. For bulk MgB_2 the thermodynamic description based on the "α-model" [18] was very successful and the two superconducting gaps extracted from the specific heat data were found in good agreement with data from tunneling spectroscopy [11]. Within this model the thermodynamic properties of a two-gap (or two-band) superconductor are calculated based on a superposition of contributions from the carriers of the two contributing bands assuming a BCS-like temperature dependence [12] for each of the two gaps of different magnitude but with the same critical temperature, T_c. The validity of the α-model as a first approximation to determine the superconducting gaps of MgB_2 has been demonstrated recently [19]. It was successfully used to determine the change of the gap structure in neutron irradiated [20] or Al substituted MgB_2 [21].

The specific heat was measured for nano crystalline and bulk MgB_2. The lattice contribution was subtracted from the data by extrapolating the high-temperature specific heat to zero T and maintaining the entropy balance of the superconducting state. The electronic specific heat as a function of the reduced temperature is shown for the nano crystalline and bulk MgB_2 samples as full and open symbols in Fig. 4. The significant difference in the temperature dependence indicates the intrinsically different superconducting gap structure of both samples. Using the α-model to fit the experimental data for bulk MgB_2 the estimated gap values of Δ_σ=6.9 meV and Δ_π=1.93 meV are in excellent agreement with previous reports from specific heat and tunneling spectroscopy. For nano crystalline MgB_2, however, the fit of the two-gap α-model leads to a σ-band gap that is considerably reduced (Δ_σ=3.77 meV) whereas the π-gap slightly increased to Δ_π=1.99 meV. In addition, there is a re-distribution of weight in that almost 2/3 of the weight contributing to the heat capacity of the nano crystalline sample results from the σ-band as compared to a 1:1 distribution in bulk MgB2.

The current data show a similar change of the superconducting gap values as has been reported for neutron-irradiated and Al-substituted MgB_2 samples [20, 21]. In both cases the larger σ-gap is reduced by either introducing defects or by replacing Mg with Al whereas the effect on the smaller π-gap is relativelt small. A correlation has been established between T_c and the value of Δ_σ. This correlation appears to be universal in that T_c decreases linearly with Δ_σ and it holds well for most of the substituted and irradiated samples [20, 21, 22]. Our values for T_c (33 K) and Δ_σ (3.8 meV) of nanocrystalline MgB_2 are consistent with the reported data and with the results of a two-band Eliashberg theory calculation correlating the T_c of $Mg_{1-x}Al_xB_2$ with the ratio of the two superconducting gaps, Δ_π/Δ_σ [23]. The origin of the σ-gap suppression in the ball-milled nanocrystalline MgB_2 samples has yet to be resolved. Two physical mechanisms, the band filling effect and the increase of interband scattering, and their effects on the gap structure of Al or carbon substituted MgB_2 have recently been proposed [24]. Whereas both effects lead to a decrease of the σ-gap their influence on the smaller π-gap is opposite. The change of band filling decreases the π-gap but the interband scattering tends to increase the smaller gap. Both mechanisms may actually compete with one another explaining the opposite tendency of the measured π-gaps in Al and carbon substituted MgB_2. The dominating physical mechanism in substituted MgB_2 is still a matter of controversy [25]. For our nanocrystalline samples of MgB_2 it appears conceivable that the filling of the bands is not changed by the synthesis procedure since there is no apparent doping that could affect the carrier density. The introduction of defects or vacancies as a consequence of stresses induced during the high-energy ball milling procedure and of a minor impurity phase (MgO and WC according to the x-ray spectra) is more likely to be the cause of the reduction of T_c and the σ-gap. The latter assumption is supported by the small increase of the π-gap and our results are similar to the case of defects introduced by neutron irradiation [20]. The current data reveal another interesting example where enhanced interband scattering in MgB_2 dominates and causes the drop of T_c as well as the characteristic change of the two superconducting gaps.

4. Summary

Nanocrystalline MgB_2 has been synthesized by high energy ball milling of MgB_2 powder. The samples show an enhanced critical current density due to improved pinning properties and a reduced T_c. The intrinsic superconducting gap structure was revealed by heat capacity measurements. The data can be described by the two-band α-model. The larger σ-gap is reduced but the smaller π-gap slightly increases as a result of the synthesis process. The results show that the interband scattering is enhanced due to defects introduced by the ball milling process.

Acknowledgments

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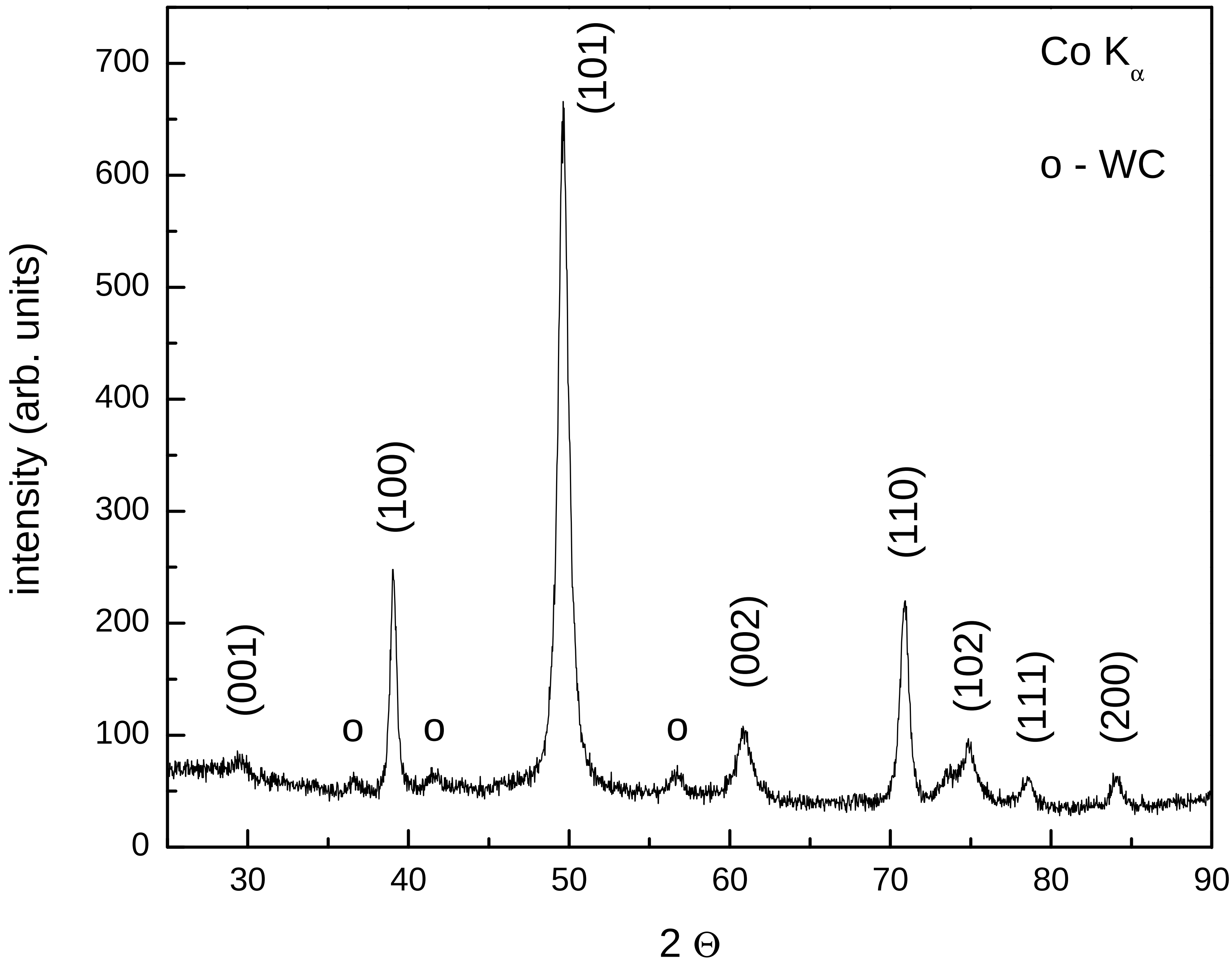
Figure 1. X-ray spectrum of nanocrystalline MgB_2 synthesized by high-energy ball milling and subsequent heat treatment. Small peaks of a minor impurity phase of WC are indicated in the spectrum.

Figure 2. Resistivity and ac-susceptibility (inset) of nanocrystalline MgB_2. The sharp transitions at T_c=33 K prove the uniformity of the sample.

Figure 3. Thermoelectric power of nanocrystalline MgB_2. Its temperature dependence and magnitude are comparable to bulk MgB_2.

Figure 4. Electronic heat capacity for nanocrystalline (closed symbols) and bulk (open symbols) MgB_2. The lines show the fit to the α-model. Note that the entropy balance is fulfilled in both data sets.


intensity (arb. units)
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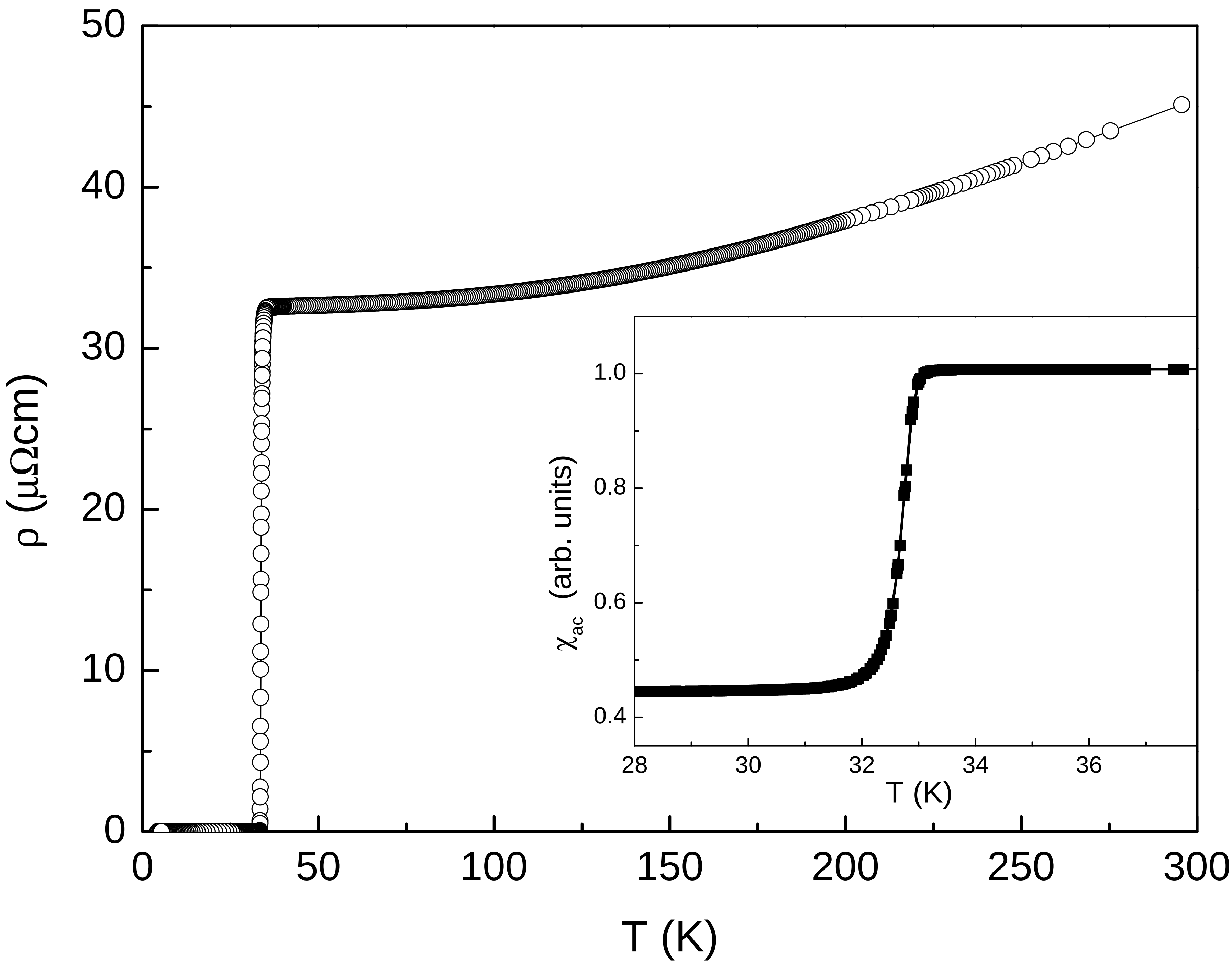

50
40
30
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0
ρ (μΩcm)
0
50
100
150
200
250
300
T (K)
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0.6
0.4
χac (arb. units)
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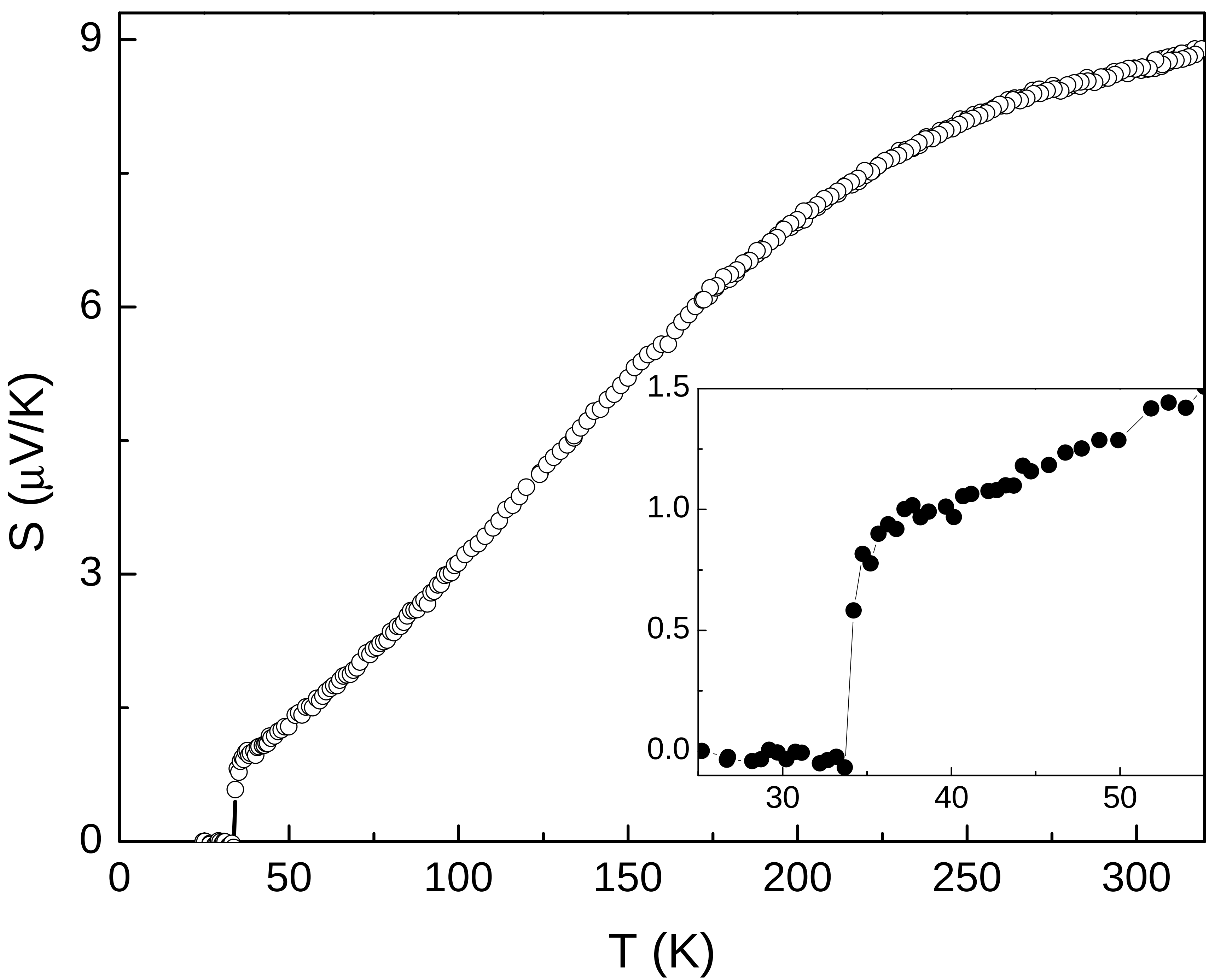
30
32
34
36
T (K)



S (μV/K)
T (K)
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100
150
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1.5
1.0
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30
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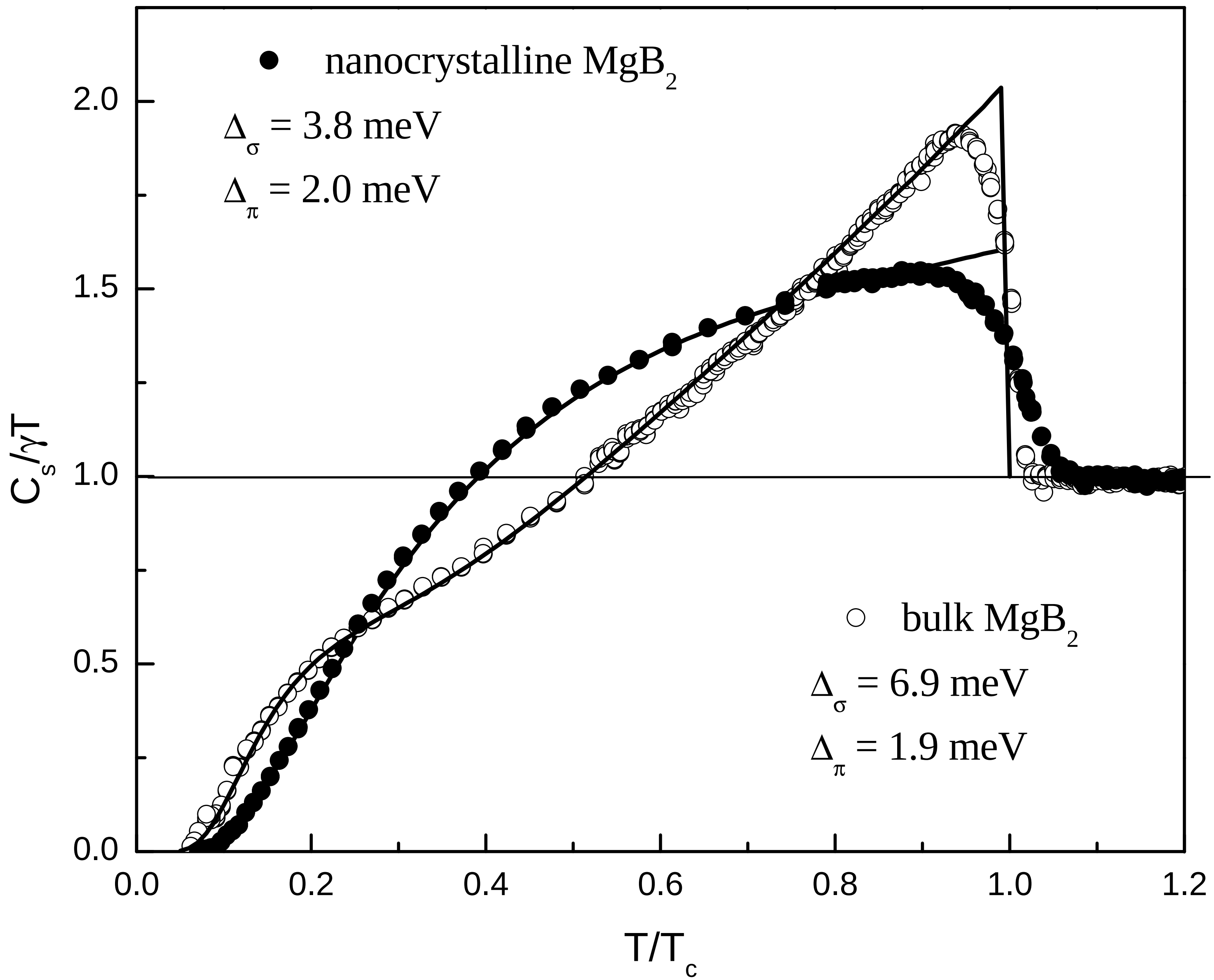
nanocrystalline MgB_2
Δ_σ = 3.8 meV
Δ_π = 2.0 meV
bulk MgB_2
Δ_σ = 6.9 meV
Δ_π = 1.9 meV
$C_s/\gamma T$
T/T_c
0.0
0.5
1.0
1.5
2.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2